THE EFFECT OF HYDROCHLORIC ACID ON THE OXIDATION OF STANNOUS CHLORIDE WITH AIR.

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The catalytic effects of many substances on the oxidation of stannous chloride in hydrochloric acid solution by means of free oxygen were studied by S. W. Young.[1] The present research was undertaken to know the effect of hydrochloric acid on the oxidation of stannous chloride with air more precisely by a new method in connection with the study on the effect of sodium hydroxide.[2] The experimental procedure is quite the same with that described in the previous paper.[3]

In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, which is equivalent to the quantity of stannous chloride; k_1 was calculated by $k_1=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=o$; $\frac{k_2}{2.303}$ was calculated by $\frac{k_2}{2.303}=\frac{1}{t}\log\frac{v_0}{v}$ and $v_{calc.}$ was obtained by $v_{calc.}=v_0-k_1 t$ or $v_{calc.}=v_0 e^{-k_2 t}$ using the mean value of k_1 or k_2.

TABLE 1.

Temp.=20°C. Air=7.78 litres per hour.

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.00647	0	12.75	—	—	—
	60	11.68	11.74	—	0.000635
	120	10.71	10.81	—	0.000631
	150	10.32	10.37	—	0.000612
	0	13.59	—	—	—
	60	12.54	12.51	—	0.000582
	90	11.99	12.00	—	0.000604
	0	17.85	—	—	—
	60	16.40	16.43	—	0.000613
	90	15.82	15.77	—	0.000583
	150	14.86	14.41	—	0.000530
				—	mean: 0.000599

(1) Young, *J. Am. Chem. Soc.*, **23** (1901), 119 & 450.
(2) S. Miyamoto, this journal, **2** (1927), 155.
(3) S. Miyamoto, ibid.

TABLE 1. (*Continued.*)

Temp. = 20°C. Air = 7.78 litres per hour.

C HCl normal	t min.	v c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.07117	0	12.17	—	—	—
	60	10.65	10.54	—	0.000963
	90	9.78	9.81	—	0.00106
	120	9.40	9.13	—	0.000935
	150	8.62	8.50	—	0.000999
	0	16.99	—	—	—
	60	14.68	14.72	—	0.00106
	90	13.49	13.70	—	0.00111
	150	11.55	11.86	—	0.00112
					mean: 0.00104
0.09672	0	11.56	—	—	—
	60	9.98	9.98	—	0.00106
	120	8.84	8.63	—	0.000971
	150	7.88	8.02	—	0.00111
	0	17.66	—	—	—
	60	15.50	15.25	—	0.000945
	100	13.69	13.84	—	0.00111
	160	11.61	11.95	—	0.00114
					mean: 0.00106
0.1359	0	12.01	—	—	—
	40	10.51	10.42	—	0.00145
	80	8.88	9.04	—	0.00164
	120	7.51	7.85	—	0.00170
	0	18.43	—	—	—
	60	15.19	14.90	—	0.00140
	80	13.96	13.88	—	0.00151
	120	12.10	12.04	—	0.00152
					mean: 0.00154
0.1682	0	7.52	—	—	—
	90	4.20	—	0.0369	0.00281
	0	12.73	—	—	—
	60	8.78	—	0.0658	0.00269
	120	6.01	—	0.0560	0.00272
	0	12.33	—	—	—
	70	7.73	—	0.0657	0.00290
	0	18.07	—	—	—
	30	15.83	—	0.0747	0.00192
	60	13.82	—	0.0708	0.00194
	90	11.14	—	0.0770	0.00233

TABLE 1. (*Continued.*)

Temp. = 20°C. Air = 7.78 litres per hour.

C HCl normal	t min.	v c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.3235	0	10.47	—	—	—
	20	8.39	8.35	0.104	—
	30	7.24	7.29	0.108	—
	50	5.04	5.17	0.109	—
	0	17.13	—	—	—
	40	12.65	12.89	0.112	—
	0	18.41	—	—	—
	15	16.87	16.82	0.103	—
	35	14.55	14.70	0.110	—
	50	13.66	13.11	0.0950	—
				mean: 0.106	
0.4587	0	11.13	—	—	—
	30	7.90	7.59	0.108	—
	40	6.74	6.41	0.110	—
	60	4.30	4.05	0.114	—
	0	17.21	—	—	—
	10	15.96	16.03	0.125	—
	20	14.85	14.85	0.118	—
	40	12.01	12.49	0.130	—
				mean: 0.118	
0.8151	0	11.84	—	—	—
	20	9.32	9.48	0.126	—
	30	8.10	8.30	0.125	—
	60	4.64	4.76	0.120	—
	0	18.02	—	—	—
	15	16.36	16.25	0.111	—
	25	15.14	15.07	0.115	—
	50	12.51	12.12	0.110	—
				mean: 0.118	

TABLE 1. (*Continued.*)

Temp.=20°C. Air=7.78 litres per hour.

C HCl normal	t min.	v c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
1.360	0	11.64	—	—	—
	15	9.88	9.91	0.117	—
	30	8.31	8.19	0.111	—
	45	6.96	6.46	0.104	—
	0	12.28	—	—	—
	15	10.53	10.55	0.117	—
	20	9.97	9.98	0.116	—
	45	7.38	7.10	0.109	—
	0	18.18	—	—	—
	40	13.23	13.58	0.124	—
	50	12.18	12.43	0.120	—
				mean: 0.115	
1.811	0	11.84	—	—	—
	20	9.12	9.20	0.136	—
	30	7.87	7.88	0.132	—
	40	6.60	6.56	0.131	—
	50	5.19	5.24	0.133	—
	0	18.18	—	—	—
	30	14.34	14.22	0.128	—
	50	11.68	11.58	0.130	—
				mean: 0.132	
2.262	0	12.66	—	—	—
	15	10.53	10.57	0.142	—
	30	8.58	8.49	0.136	—
	45	6.31	6.40	0.141	—
	50	5.70	5.71	0.139	—
	0	18.28	—	—	—
	30	14.08	14.11	0.140	—
	70	8.85	8.55	0.135	—
				mean: 0.139	

TABLE 2.

Temp.=30°C. Air=7.78 litres per hour.

C HCl normal	t min.	v c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.00670	0	13.94	—	—	—
	60	12.37	—	0.0262	0.000865
	80	11.99	—	0.0244	0.000818
	150	10.60	—	0.0223	0.000793
	0	17.81	—	—	—
	50	16.43	—	0.0276	0.000700
	90	15.70	—	0.0234	0.000608
	140	14.68	—	0.0224	0.000600
0.1407	0	11.92	—	—	—
	26	9.80	—	0.0815	0.00327
	45	8.63	—	0.0731	0.00312
	80	7.05	—	0.0609	0.00285
	0	19.17	—	—	—
	20	17.20	—	0.0985	0.00235
	40	15.40	—	0.0943	0.00238
	70	14.28	—	0.0699	0.00183
0.2077	0	11.43	—	—	—
	20	9.30	—	0.107	0.00448
	40	7.48	—	0.0988	0.00460
	60	6.20	—	0.0872	0.00443
	0	18.26	—	—	—
	20	15.87	—	0.120	0.00305
	30	13.51	—	0.119	0.00327
	60	11.91	—	0.106	0.00309
0.2605	0	10.89	—	—	—
	15	8.91	8.97	0.132	—
	30	6.99	7.05	0.131	—
	45	5.45	5.13	0.121	—
	0	17.42	—	—	—
	15	15.60	15.50	0.121	—
	30	13.40	13.58	0.134	—
	45	11.50	11.66	0.131	—
				mean: 0.128	
0.3417	0	10.85	—	—	—
	15	9.00	9.03	0.123	—
	30	7.47	7.22	0.113	—
	45	5.92	5.40	0.110	—
	0	16.36	—	—	—
	15	14.32	14.54	0.136	—
	30	12.71	12.73	0.122	—
	45	11.00	10.91	0.119	—
				mean: 0.121	

TABLE 2. (*Continued.*)

Temp.=30°C. Air=7.78 litres per hour.

C HCl normal	t min.	v c.c.	v calc. c.c.	k_1	$\frac{k_2}{2.303}$
0.4297	0	12.34	—	—	—
	15	10.28	10.27	0.137	—
	30	8.32	8.20	0.134	—
	45	6.25	6.13	0.135	—
	0	18.78	—	—	—
	15	16.70	16.71	0.139	—
	30	14.45	14.64	0.144	—
	45	12.56	12.57	0.138	—
				mean: 0.138	
0.8527	0	12.47	—	—	—
	15	10.55	10.59	0.128	—
	20	10.03	9.97	0.122	—
	30	8.93	8.72	0.118	—
	45	6.62	6.84	0.130	—
				mean: 0.125	
1.276	0	11.89	—	—	—
	15	10.16	10.13	0.115	—
	20	9.49	9.55	0.120	—
	30	8.40	8.38	0.116	—
	45	6.73	6.62	0.115	—
				mean: 0.117	
1.699	0	12.47	—	—	—
	15	10.38	10.44	0.139	—
	20	9.77	9.77	0.135	—
	30	8.40	8.42	0.136	—
	45	6.64	6.39	0.130	—
				mean: 0.135	
2.122	0	12.19	—	—	—
	15	10.01	10.12	0.145	—
	20	9.45	9.43	0.137	—
	30	8.12	8.05	0.136	—
	45	6.16	5.99	0.134	—
				mean: 0.138	

TABLE 3.

Temp.=40°C. Air=7.78 litres per hour.

C HCl normal	t min.	c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.00670	0	12.41	—	—	—
	40	11.37	—	0.0260	0.000950
	80	10.75	—	0.0208	0.000780
	120	9.86	—	0.0213	0.000832
	0	19.00	—	—	—
	40	17.62	—	0.0345	0.000819
	80	16.94	—	0.0258	0.000623
	120	15.99	—	0.0251	0.000624
0.04020	0	12.44	—	—	—
	40	10.87	—	0.0393	0.00146
	80	10.04	—	0.0300	0.00116
	120	9.37	—	0.0256	0.00103
	0	18.35	—	—	—
	50	16.37	—	0.0396	0.000992
	80	15.65	—	0.0338	0.000864
	130	14.90	—	0.0265	0.000696
0.0737	0	11.30	—	—	—
	40	9.56	—	0.0435	0.00182
	80	8.10	—	0.0400	0.00181
	120	7.57	—	0.0311	0.00145
	0	18.72	—	—	—
	40	16.43	—	0.0573	0.00142
	80	14.80	—	0.0490	0.00128
	120	13.74	—	0.0415	0.00112
0.0913	0	11.42	—	—	—
	40	9.44	—	0.0495	0.00207
	80	8.21	—	0.0401	0.00179
	120	7.41	—	0.0334	0.00157
	0	17.82	—	—	—
	40	15.28	—	0.0635	0.00167
	80	13.63	—	0.0524	0.00146
	120	12.63	—	0.0423	0.00125

TABLE 3. (*Continued.*)

Temp.=40°C. Air=7.78 litres per hour.

C HCl normal	t min.	v c.c.	v *calc.* c.c.	k_1	$\frac{k_2}{2.303}$
0.1407	0	12.54	—	—	—
	25	10.33	—	0.0884	0.00337
	50	8.92	—	0.0724	0.00296
	75	7.84	—	0.0627	0.00272
	0	18.14	—	—	—
	25	15.49	—	0.106	0.00274
	50	13.76	—	0.0876	0.00740
	75	12.50	—	0.0752	0.00216
0.2077	0	12.11	—	—	—
	20	9.63	—	0.124	0.00498
	40	7.79	—	0.108	0.00479
	60	6.35	—	0.0960	0.00467
	0	18.95	—	—	—
	20	16.22	—	0.137	0.00338
	40	13.96	—	0.125	0.00332
	60	12.04	—	0.115	0.00328
0.2605	0	12.39	—	—	—
	15	10.17	10.14	0.148	—
	30	8.00	7.89	0.146	—
	45	6.23	5.64	0.137	—
	0	18.52	—	—	—
	15	16.12	16.27	0.160	—
	30	13.84	14.02	0.156	—
	45	11.68	11.77	0.152	—
				mean: 0.150	
0.3417	0	11.62	—	—	—
	15	9.81	9.70	0.121	—
	30	7.88	7.78	0.125	—
	45	6.10	5.86	0.123	—
	0	18.89	—	—	—
	15	16.88	16.97	0.134	—
	30	15.01	15.05	0.129	—
	45	12.84	13.13	0.134	—
				mean: 0.128	

TABLE 3. (*Continued.*)

Temp.=40°C. Air=7.78 litres per hour.

C HCl norma	t min.	v c.c.	v. *calc.* c c.	k_1	$\frac{k_2}{2.303}$
0.4297	0	11.82	—	—	—
	15	9.64	9.66	0.145	—
	20	9.02	8.94	0.140	—
	30	7.33	7.50	0.150	—
	45	5.43	5.34	0.142	—
				mean: 0.144	
0.8527	0	12.07	—	—	—
	16	9.98	9.96	0.131	—
	20	9.41	9.43	0.133	—
	30	8.13	8.11	0.131	—
	46	6.01	6.00	0.132	—
				mean: 0.132	
1.276	0	11.63	—	—	—
	15	9.50	9.50	0.142	—
	20	8.79	8.79	0.142	—
	30	7.34	7.37	0.143	—
	45	5.33	5.24	0.140	—
				mean: 0.142	
1.699	0	11.97	—	—	—
	15	9.66	9.67	0.154	—
	20	8.97	8.91	0.150	—
	30	7.29	7.38	0.156	—
	45	5.13	5.08	0.152	—
				mean: 0.153	
2.122	0	11.94	—	—	—
	15	9.65	9.58	0.153	—
	20	8.90	8.80	0.152	—
	30	7.12	7.23	0.161	—
	45	4.68	4.87	0.161	—
				mean: 0.157	

As is seen in Table 1, 2 and 3, the oxidation velocity is independent of the concentration of stannous chloride when the concentration of hydrochloric acid is greater than about 0.25 normal under the condition of this experiment. This can be explained by the assumption that the oxidation velocity thus measured is no other than the dissolution velocity of oxygen into the solution.

When the concentration of hydrochloric acid is smaller than about 0.25 normal, the reaction seems to be between first and zero order. The concentration of hydrochloric acid, the initial values of which are given in the tables, can not be considered to be constant during the reaction; it decreases by the formation of stannic chloride. The decrease is not negligible when the concentration is smaller than about 0.25 normal, for in this region the oxidation velocity of stannous chloride increases rapidly with the increase of the concentration of hydrochloric acid. This will be one of the causes of the decrease of the values of k_1 or k_2 in Table 2 and 3 with time when the concentration of hydrochloric acid is small.

Anyhow from the above results it can be said that the oxidation velocity of stannous chloride increases rapidly with the increase of the concentration of hydrochloric acid, until it reaches the dissolution velocity of oxygen into the solution, which is almost constant when the concentration of hydrochloric acid is greater than about 0.25 normal under the condition of this experiment.

By comparing Table 1, 2 and 3, it can be said that the effect of temperature on the reaction is small.

The Dissolution Velocity of Oxygen into Hydrochloric Acid Solution. The approximate values of the dissolution velocity of oxygen into hydrochloric acid of various concentrations, when air was passed into 40 cc. of the solution in a test tube (diameter = 3 cm.) through a glass tube (inside diameter = 4 mm., outside diameter = 6 mm.) at the rate of 7.78 litres per hour, were calculated from the above results.

The dissolution velocity, given in Table 4, when the concentration of hybrochloric acid is zero, was calculated from the oxidation velocity of sodium sulphite with air.[1] As is seen in Table 4 the dissolution velocity of oxygen into water decreases rapidly by adding hydrochloric acid until the concentration of hydrochloric acid reaches about 0.25 normal, and further addition of hydrochloric acid has almost no effect on the dissolution velocity, which is smaller than that into sodium hydroxide solution, calculated quite the same way in the previous paper.[2]

(1) S. Miyamoto, this journal, **2** (1927), 74.
(2) S. Miyamoto, ibid., **2** (1927), 158.

TABLE 4.

Temp.	C HCl normal	k_1	Dissolution velocity of oxygen $\times 10^6$ mols per minute
20°C.	0	0.330	8.2
	0.3235	0.106	2.6
	0.4587	0.118	2.9
	0.8151	0.118	2.9
	1.360	0.115	2.9
	1.811	0.132	2.3
	2.262	0.139	3.5
30°C.	0	0.345	8.6
	0.2605	0.128	3.2
	0.3417	0.121	3.0
	0.4297	0.138	3.4
	0.8527	0.125	3.1
	1.276	0.117	2.9
	1.699	0.135	3.4
	2.122	0.138	3.4
40°C.	0	0.382	9.6
	0.2605	0.150	3.7
	0.3417	0.128	3.2
	0.4297	0.144	3.6
	0.8527	0.132	3.3
	1.276	0.142	3.5
	1.699	0.153	3.8
	2.122	0.157	3.9

Summary.

1. The oxidation velocity of stannous chloride in hydrochloric acid with air was studied. When the concentration of hydrochloric acid is smaller than about 0.25 normal, the reaction seems to be between first and zero order. When the concentration of hydrochloric acid is greater than about 0.25 normal, the velocity is independent of the concentration of stannous chloride.

2. The effect of temperature is small.

3. The dissolution velocity of oxygen into hydrochloric acid of various concentrations was obtained indirectly.

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FORMATION OF THE RADIOACTIVE MANGANIFEROUS DEPOSITS FROM TANOKAMI, AND THE SOURCE OF MANGANESE IN THE DEEP-SEA MANGANESE NODULES.[1]

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In the previous paper[2] it has been shown that the feebly radioactive manganiferous deposit from the Tanokami district, Oomi Province, occurs in two modes, one in irregular masses charging narrow cracks of the hill-side rock, and the other in small nodular forms as one of the pebbly constituents of the gravel-beds of a stream. Both of them leave, on treatment with hydrochloric acid, a considerable residue of quartz grains with a large amount of faint yellowish green clayey matter. It so happens on close examination that this residue is practically identical with the fragments of rock body on the hill side, through which the deposit is disseminated. The rock, with which this manganiferous deposit is so intimately associated, seems to be consisted essentially of a kind of altered granitic rock, a marked feature being the presence of the above stated greenish clayey matter.

Similar manganese nodules, hitherto reported, have chiefly been found on the bottom of the deep sea and sometimes of particular creeks or rivers. The following will probably be the conspicuous cases so far as known, namely, those from the beds of Pacific Ocean[3] and of Loch Fyne in Scotland[4], from Onybygambach, New South Wales[5], and those found in Mesozoic deep-sea deposit from Borneo, Timor and Rotti[6], and on the bed of the River Vistula[7]. All of these nodules are in accord with one another in respect of being largely composed of insoluble siliceous gangue and constantly containing a tolerable amount of iron besides manganese in the black portion soluble in hydrochloric acid. The proportion of the gangue varies of course considerably, but the composition of the soluble part is

(1) Read before the Annual Meeting of the Chemical Society of Japan, April 5, 1927.

(2) This journal, **1** (1926), 43.

(3) J. Gibson, "Challenger Rept. Deep-Sea Deposits," (1891), 417–423; F. W. Clarke, "The Data of Geochemistry," (1924), 135. (Challenger Collection).
A. Agassiz, *Am. J. Sci.*, [4] **9** (1900), 33. (Albatross Collection).

(4) J. Y. Buchanan, *Chem. News*, **44** (1881), 253; *Proc. Roy. Soc. Edinburgh*, **18** (1890), 19.

(5) W. M. Doherty, *Australasian Assoc. Adv. Sci.*, **6** (1898), 339; *Am. J. Sci.*, [4], **9** (1900), 72.

(6) G. A. F. Molengreaff, *Proc. Roy. Acad. Amsterdam*, **18** (1915), 415; cf. "Neues Jahrb. Min. Geol"., (1916), II 233.

(7) E. Dittler, Tsch. Min. Mitt., **36** (1924), 164: cf. *J. Chem. Soc.*, **128** (1925), Abs. (ii), 322.

generally in close analogy in different sorts. The radium content of the nodules, however, has not been determined by the former investigators, except the ones from the bed of Pacific Ocean.[1] For the comparison of the chemical constituents, therefore, the original analyses by J. Gibson[2] and by J. Joly[3] made on the oceanic nodules from the Pacific Ocean, as well as that of the Tanokami nodules previously made by the author[4] are reproduced in the following tables.

Analyses of the soluble portion of the nodules.

Constituents / Nodules from	MnO_2 & MnO	Fe_2O_3	Al_2O_3	PbO	CuO	ZnO NiO CoO	CaO	MgO	H_2O	Tl_2O	Acidic oxides	Total
The Tanokami Hill, Japan. (4)	59.8	14.6	9.9	4.8	(small)	3.7	—	—	7.2	—	—	(100)
The Pacific Ocean. (2)	52.4	27.0	6.3	0.1	0.7	2.7	4.0	4.6	—	0.06	2.0*	99.0

* MoO_3, V_2O_5, P_2O_5, SO_3, CO_2.

Amount of radium in the nodules

Manganese nodules from	Variety.	Amount of the insol. gangue. %	Radium content	
			Ra per gr. of the material. gr.	Ra per gr. of the soluble portion. gr.
Tanokami[4]	The hill-side deposit.	89.7	131×10^{-12}	1640×10^{-12}
	The river nodule.	68.9	115	388
Pacific Ocean[3]	Nodule, collected at a depth of 2750 fathoms.	16.0	24	29
	" " " " " 2370 fathoms. (off W. Coast of S. America.)	17.9	21	26

Although the two differ in certain particulars, as in lime, magnesia, thallia and acidic oxides, yet the general correspondence is remarkably close, and the presence of minor constituents, such as lead, copper, zinc, nickel, cobalt and radium, is strikingly harmonious. As regards the

(1) J. Joly, *Phil. Mag.*, **16** (1908), 190.
(2) Loc. cit.
(3) Loc. cit.
(4) Iimori, loc. cit.

content of radium in the Tanokami nodules, attention has already been directed to the fact that the irregular masses of the manganiferous deposit occurring on the hill-side carry more radium than that in the nodules existing on the river bed, viz. the amount of radium in the former being about four times as much as that in the latter. This fact is possibly to be ascribed to the leaching action of stream water. The far less content of radium in the oceanic nodules will, therefore, be so explained that they have lost the greater part of the radium or uranium while lying on the bottom of the deep sea through a long period of geological time, and yet, as will be seen in the above figures, the richness in radium of the oceanic manganese nodules is obviously greater than that which we are aware of the rocks on the land, the average values being 1.7×10^{-12} and 1.1×10^{-12} grams radium per gram for igneous and sedimentary rocks respectively.[1]

Regarding the source of manganese which constitutes the deep sea nodules, no opinion seems yet to be substantially decisive. G. W. Gümbel supposes that the manganese is derived from submarine springs.[2] J. Murray attributes it to the product of the subaqueous decomposition of volcanic débris.[3] J. Y. Buchanan[4] and others[5] solely regard as due to the manganese dissolved in the sea water. Being formed, however, of the manganese universally dissolved, usually contained but in trace, in the sea water, the nodules would be found in everywhere of the bottom of the sea. But, in fact, such a mode of distribution has never been observed, and its sporadic occurrence in the bottom of the deep sea or special creeks shows, I suppose, that the manganese may probably be derived from certain manganese minerals, possibly peculiar ferromanganese minerals containing uranium, locally cropped out on the ocean floor.

Hence it will be so explicable that the manganese deposits from the Tanokami district should be formed by the same process as the cases of the sea nodules. While the region of the Tanokami hill and the neighbourhood had, once in early ages, been lying beneath the water, the veins and dykes of granitic pegmatite including the original manganese and iron bearing radioactive minerals, for instance, such as wolframite which is now sometimes found in this district in small quantity, were subjected to the aqueous alteration. Some of the constituents such as manganese, iron etc.

(1) A. Z. Eve and D. Mc Intosh, *Phil. Mag.*, [6], **14** (1907), 231.
(2) *Jahr. Min.*, (1876), 869; cf. *J. Chem. Soc.*, **38** (1880), Abs., 16.
(3) *Proc. Roy. Soc. Edinburgh*, **9** (1876), 255; cf. *Bull. U. S. Geol. Survey*, **770** (1924), 135.
(4) *Proc. Roy. Soc. Edinburgh*, **18** (1890), 17; cf. *J. Chem. Soc.*, **60** (1891), Abs., 994.
(5) J. B. Boussingault, *Ann. Chim. Phys.*, (5) **27** (1882), 289; L. Dieulafait, *Compt. rend.*, **96** (1883), 718; R. Irvine and J. Gibson, *Proc. Roy. Soc. Edinburgh*, **18** (1890), 54; cf. *J. Chem. Soc.*, **60** (1891), Abs., 995; E. Dittler, loc. cit.

of the minerals imbedded in the rock went into solution and was precipitated with radium or uranium near its points of derivation between the cracks of the rock or around any nuclei which happened to be at hand, accordingly around the fragments of the altered rock yielding the radioactive manganiferous nodules. It will therefore be thought that the formation of the Tanokami nodules would never take place unter the stream water, seen at the present time, but in the quiet depths of the sea or lake throughout the geological ages. It would be expected, accordingly, that the rock body on the hill side of the Tanokami district have come up from the deep water, and the black impregnation on the rock blocks lying on the river bed, now frequently seen, will be due to the manganese and iron derived as the result of recent weathering and erosion from the above mentioned manganiferous deposits and nodules.

Finally, one thing which is much suggestive in this connection, is the origin of the radium contained in the oceanic water and the deep-sea deposits. It has been so considered by J. Joly[1] that the oceanic radium has entirely been supplied by the rocks and minerals on the land, having been leached by the rain water and poured by rivers into the sea. It may, however, be concluded from the foregoing considerations that some parts of the oceanic radium come from certain radioactive minerals cropped out sporadically on the bottom of the sea. In this way it will also easily be accounted for the less content of radium in the river water than that in the sea water. The critical revision of radium content in all the manganese nodules known is highly desirable.

The author's thanks are due to Prof S. Tsuboi of the Geological Laboratory, Tokyo Imperial University for his kind advices given on the examination of rocks.

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(1) J. Joly, "Radioactivity and Geology," (1909), p. 54.

THE GREEN KAOLIN FROM TANOKAMI. IDENTITY OF THE UNIVERSAL MINOR CONSTITUENTS OF THE IGNEOUS ROCK WITH THE CHROMOSPHERIC ELEMENTS OF THE SUN.[1]

By **Satoyasu IIMORI.**

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The Composition of the Green Kaolin. The faint yellowish green clayey matter, which occurs almost constantly associated with the radioactive manganiferous nodules and deposits from Tanokami, Oomi Province and usually forms a part of the insoluble portion of the latter,[2] has fully been analysed. The material used for the analysis was a comparatively large lump found on the hill side, where the radioactive manganiferous deposits are disseminated. It was of an amorphous character and not perfectly homogeneous. The specific gravity was determined as 2.71 with a hardness of about 2.5~3.5, and the streak was white. It gave the result of the second column in the following table, the third to the sixth showing the compositions of the various species of kaolin for the purpose of comparison.

Constituents	Analysis of the material. (%)	Kaolinite (monocl.)	Rectonite (amorph.)	Catlinite (amorph.)	Pyrophyllite (monocl.)
Loss on ignition $<130°$	0·23	$Al_2O_3 \cdot 2SiO_2$	$Al_2O_3 \cdot 2SiO_2$	$Al_2O_3 \cdot 3SiO_2$	$Al_2O_3 \cdot 4SiO_2$
Loss on ignition $>130°$	3·56	$2H_2O$	H_2O	H_2O	H_2O
SiO_2	58·01	46·5	50·0	60·0	67·0
Al_2O_3	35·79	39·5	42·5	34·0	28·0
Fe_2O_3	1·32		including Halloysite, Newtonite, $Al_2O_3 \cdot 2SiO_2 \, xH_2O$.		including Montmorillonite, $Al_2O_3 \cdot 4SiO_2 \, xH_2O$.
FeO	1·10				
Mn_3O_4	0·083				
Rare earths	0·040				
MgO	0·014				
(Total)	100·15	$\left(\frac{SiO_2}{Al_2O_3}=2\right)$	(„ =2)	(„ =3)	(„ =4)

The analysis clearly shows, setting aside the iron and other minor constituents, the character of this material as a kind of kaolin which has,

(1) Read before the Annual Meeting of the Chemical Society of Japan, April 5, 1927.
(2) This journal, **1** (1926), 43.

however, neither composition of a kaolinite nor of a pyrophyllite but of the so-called catlinite. According to the descriptions cited in Dana's Mineralogy,[1] the latter is said to be no definite mineral species and pink in colour. The material analyzed is of a greenish colour, but its composition is in quite accord with that of the catlinite, the analysis nearly satisfying the formula $Al_2O_3 \cdot 3SiO_2 \cdot H_2O$.

The noteworthy feature of this kaolin is its containing a small quantity of rare earths which chiefly consist of the yttrium group. Examining spectrographically it shows that the rare earths separated contain a small amount of the terbium group and almost no member of the cerium group. The following indicate the partial analyses of rare earths.

The material taken. (gr.)	Rare earths found		Scandia separated from the rare earths obtained	
	(mg.)	(%)	(mg.)	(%)
28.60	13.2	0.046	0.096 (a)	0.00034
27.77	8.1	0.034	(<0.19) (b)	(<0.00080)

For the determination of the terbium earths, 0.0189 gr. of oxides of the rare earths freed from scandia was used. It gave 0.00146 gr. of oxides of the terbium group with a trace of the cerium group, both having been separated as the insoluble double potassium sulphates. The results is therefore represented as follows: 0.037% yttrium earths, 0.003% terbium earths, corresponding to 7.73% of the total rare earths, and less than 0.000x% scandia.

As to the carring out of the separation of the rare earths from the material, the following procedure was mainly employed as prescribed by W. F. Hillebrand.[2] The sample was first fused with fusing mixture. Eliminating silica and then heavy metals of the hydrogen sulphide group which were contained in small amounts, the rare earths with iron were precipitated by caustic potash. The precipitates thus obtained were treated with hydrofluoric acid so as to keep the iron, manganese, titanium, etc. in solution. The insoluble residue, mainly consisting of the fluorides of the whole rare earths, was decomposed with sulphuric acid in excess. The rare earths were then repeatedly precipitated by means of oxalic acid, after the sulphates have been dissolved in dilute hydrochloric acid. The oxalates were ignited for the oxides and weighed.

(1) E. S. Dana, "System of Mineralogy," IV Edition, p. 696.

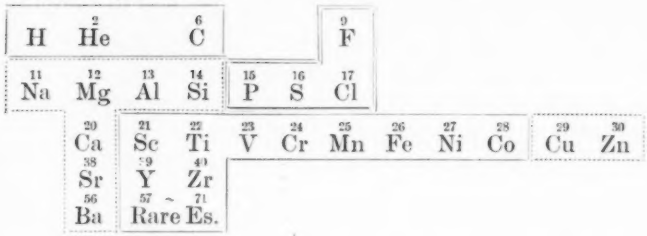
(1) *Bull. U. S. Geolog. Survey*, 700 (1919), 176.

To separate the scandium, the oxides of rare earths obtained were dissolved in hydrochloric acid. The excess of acid was removed by evaporation, and the scandium was precipitated as basic thiosulphate by the addition of 30 per cent sodium thiosulphate solution. The figure indicated with the mark (a) in the foregoing table was obtained according to P. and G. Urbain's process,[1] the scandium finally having been precipitated as phosphate by ammonium phosphate after the basic thiosulphate has been dissolved in hydrochloric acid and evaporated up to dryness. Another figure marked with (b) was tentatively obtained, roughly weighing the ignition product of the basic thiosulphate as crude oxide, as the precipitate yielded on the addition of sodium thiosulphate was too small.

The fractions obtained in the course of a duplicate analysis were examined spectroscopically using a large quartz spectrograph on Littrow mounting. The rare earth fraction showed the bulk of lines, including the whole principal lines given by Exner and Haschek, of scandium, yttrium, ytterbium, dysprosium, and also abundant lines of erbium, thullium, lutecium, terbium and gadolinium. The scandium fraction separated gave rather faintly a few of its lines, but none of other elements. The sulphide fraction of heavy metals, previously precipitated by hydrogen sulphide in acidic solution, gave the lines of copper and tin. In the precipitate obtained by ammonia from the main solution, after removal of the iron and aluminium by the succinate method, besides the lines of the above mentioned rare earths, those of nickel, cobalt, zink, titanium, zirconium, niobium, chromium, molybdenum, tungsten and ruthenium were detected, and a few lines of vanadium and lithium were also observed. Roughly having been determined, these minor constituents except the rare earths, computing as oxides, hardly amounted to 0.1—0.15 per cent of the material, hence they were omitted in the foregoing table of analysis for the convenience of manifestation.

Comparison of the Minor Constituents of the Igneous Rock with the Elements in the Solar Chromosphere. One of the well known elements existing in the highly ionized state in the high level region of the solar chromosphere is the scandium which is, as stated above, distinctly detected in the rare earth fraction of the green kaolin occurring associated with the radioactive manganiferous nodules from Tanokami. The whole chromospheric elements given by F. W. Dyson[2] and S. A. Mitchell[3] are,conveniently tabulated as below, together with four other elements shown enclosed with the double lines.

(1) *Compt. rend.*, **174** (1922), 1310.
(2) *Phil. Trans. Roy. Soc.*, A, **205** (1906), 403.
(3) *Astroph. Jour.*, **38** (1913), 407.



The elements inside the single line enclosure in the above table are those which give most abundant or distinct lines in the spectrum of the chromosphere, and those inside the dotted line enclosure representing the elements which are mentioned to be observed rather faintly or in deficient numbers in the spectral lines of the chromosphere.

As a matter of fact, the elements detected in small amounts in the green kaolin and the manganiferous nodules previously descrived nearly coincide with the principal members of the chromospheric elements excepting carbon and helium, and on the other hand, with what are called the universal minor constituents of the igneous rock shown by H. S. Washington,(1) W. F. Hillebrand,(2) etc. which are nothing but those elements indicated in the above table including four more elements, phosphorus, sulphur, fluorine and chlorine. Judging from the numerous results of rock analyses, hitherto put forward by several investigators, the constant minor constituents of the majority of igneous rocks are quite particular and surely to be recognized, but why they are so universally distributed among the igneous rocks is now in dispute. As will be pointed out, however, it may be seen that the universal minor constituents of the igneous rock are in close agreement with the elements constituting the solar chromosphere, and the spectroscopical lacking in some elements such as phosphorus, sulphur, fluorine and chlorine in the chromosphere will not be serious, as they give very insignificant lines, or at times no line in their spectra.

Advocating the nebular hypothesis, when the earth was formed by cooling from a gaseous mass through the same state as the sun seen at the present time, the primeval atmosphere must have been quite unlike our present envelope, and we may suppose that it was probably the same as the present chromosphere of the sun. When the liquefaction commenced over the whole surface of the our globe in the earliest state under such an atmosphere as above, no doubt there must have been contained in the liquid crust the same elements as those in the primitive atmosphere, a hetero-

(1) H. S. Washington, "Manual of the Chemical Analysis of Rocks," (1919), p. 17.
(2) W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," (1919), p. 25.

geneous equilibrium between both phases having been established. As the temperature of the earth has decreased and the liquefaction proceeded, the composition of the gas phase would then gradually have changed, according as the atmospheric elements have passed into the liquid phase. Hence all the rocks afterwards solidified out from the original surface magma must have more or less been contaminated with all of these primeval atmospheric elements.

According to the view set out above, though we have no clear evidence for it yet, it should possibly be considered that the presence of helium in certain non-radioactive minerals such as beryl, fluorite, sphene, etc. and in some natural gases may be ascribed to this notable one of the constituents of the primeval atmosphere supposed. The present is not the place for any extended discussion, but the close analogy between the universal minor constituents of the igneous rock and the chromospheric elements, if it might be apparent, will not be denial.

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ON THE NITRILE-ESTERS OF THE DICARBOXY-GLUTACONIC ACID.

By **Yoshiyuki URUSHIBARA.**

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In the previous paper[1] dealing with the so-called diethyl dicyano-glutaconate the author showed that this substance has the composition $C_{11}H_{12}O_4N_2 \cdot \frac{1}{2}H_2O$ instead of $C_{11}H_{12}O_4N_2$, and its constitution is represented by the formula $(C_{10}H_{12}O_4N)-C(=NH)-NH-CO-(C_{10}H_{12}O_4N)$. The triethyl dicyanoaconitate $C_2H_5OOC(CN)C=C(COOC_2H_5)-CH(CN)COOC_2H_5+\frac{1}{2}H_2O$[2], and the methenylbismalonitrile-imidether $(CN)_2C=CH-CH(CN)C(NH)-OC_2H_5+\frac{1}{2}H_2O$[3], are also combined with half a molecule of water. In order to examine the presence of such a tendency as of combining with water, and at the same time expecting some interesting results which would arise from their being the derivatives of glutaconic acid, the author synthesized and investigated the following nitrile-esters of the dicarboxyglutaconic acid.

(1) This journal **2** (1927), 26.
(2) G. Errera und F. Perciabosco, *Ber.*, **34** (1901), 3704.
(3) W. Zoernig, *J. prakt. Chem.* **74** (1906), 435.

By the condensation of one of diethyl ethoxymethylene-malonate $(C_2H_5OOC)_2C=CHOC_2H_5$, ethyl ethoxymethylene-cyanoacetate $C_2H_5OOC(CN)C=CHOC_2H_5$, and ethoxymethylene-malonitrile $(CN)_2C=CHOC_2H_5$, with one of diethyl sodio-malonate $CHNa(COOC_2H_5)_2$, ethyl sodio-cyanoacetate $CHNa(CN)COOC_2H_5$, and sodio-malonitrile $CHNa(CN)_2$, nine methenyl compounds are to be formed, which are the nitrile-esters of the dicarboxyglutaconic acid. They are:

(I) Tetraethyl propylene-α, α, γ, γ-tetracarboxylate (or tetraethyl dicarboxyglutaconte), $(C_2H_5OOC)_2C=CH-CH(COOC_2H_5)_2$;

(II) Triethyl α-cyanopropylene-α, γ, γ-tricarboxylate (or triethyl α-cyano-γ-carboxyglutaconate), $(C_2H_5OOC)_2C=CH-CH(CN)COOC_2H_5$;

(III) Triethyl γ-cyanopropylene-α, α, γ-tricarboxylate, $C_2H_5OOC(CN)C=CH-CH(COOC_2H_5)_2$;

(IV) Diethyl α, α-dicyanopropylene-γ, γ-dicarboxyate, $(C_2H_5OOC)_2C=CH-CH(CN)_2$;

(V) Diethyl γ, γ-dicyanopropylene-α, α-dicarboxylate, $(CN)_2C=CH-CH(COOC_2H_5)_2$;

(VI) Diethyl α, γ-dicyanopropylene-α, γ-dicarboxylate (or diethyl dicyanoglutaconate), $C_2H_5OOC(CN)C=CH-CH(CN)COOC_2H_5$;

(VII) Ethyl α, α, γ-tricyanopropylene-γ-carboxylate, $C_2H_5OOC(CN)C=CH-CH(CN)_2$;

(VIII) Ethyl α, γ, γ-tricyanopropylene-α-carboxylate, $(CN)_2C=CH-CH(CN)COOC_2H_5$;

(IX) α, α, γ, γ-Tetracyanopropylene, $(CN)_2C=CH-CH(CN)_2$.

Of course the above condensations will give first the α-sodio-derivatives of these compounds. All of them, except (I) which is well known as the tetraethyl dicarboxyglutaconate, have never been closely investigated, and most of them have never been synthesized. Errera[1] carried out the condensation of diethyl ethoxymethylene-malonate with ethyl sodio-cyanoacetate, and the oily substance obtained by him was probably the nitrile-ester (II), but with no analytical determination of its composition, he transformed it into the diethyl dihydroxydinicotinate. The compound which had been considered to be the diethyl α, γ-dicyanopropylene-α, γ-dicarboxylate (VI), the so-called diethyl dicyanoglutaconate, was clearly explored by the author as stated above. The compound obtained by Zoernig[2] in the condensation of malonitrile, chloroform, and sodium ethylate was not the tetranitrile (IX), but its imidether semihydrate.

The first two compounds (I) and (II) are not described in this paper, because the tetraethyl dicarboxyglutaconate had no important relation to the

(1) *Ber.*, **31** (1898), 1243.
(2) Loc. cit.

present investigation, and the triethyl α-cyanopropylene-α, γ, γ-tricarboxylate had been synthesized by Errera if not in a satisfying manner. The present author has synthesized the other seven compounds, or, strictly speaking, performed the seven condensations which would give the seven compounds.

The general procedure of the condensations of the ethoxymethylene compounds with sodium compounds was very simple.[1] These reactions proceeded smoothly at the ordinary temperature in the absolute alcoholic solutions. The resulting solutions of the sodium derivatives of the methenyl compounds were coloured more or less deep red, but, besides the inevitable formation of the colouring by-product which might be very small in quantity, no side reactions seemed to occur. On evaporating the alcohol in vacuo over sulphuric acid (heating was avoided in fear of any secondary reaction) the solutions left the crystalline mass of the sodium compounds. As these sodium compounds are generally easily soluble in water, a considerable loss could not be avoided in the recrystallisation from water.

Some of the sodium compounds were obtained in coloured appearance, and others in colourless state. From the analogy of the constitution all of them should be colourless and the colours of some of them must be due to impurities which can be difficultly removed.

(III) **Triethyl γ-cyanopropylene-α, α, γ-tricarboxylate.** Sodium was dissolved in absolute alcohol, and diethyl malonate was added. Ethyl ethoxymethylene-cyanoacetate in powder was added to this solution under cooling in ice water. The solution became red, and on evaporating the alcohol in vacuo over sulphuric acid, a coloured crystalline mass was obtained. After washing with ether the crystals were again dried over sulphuric acid. This crystalline sodium compound, triethyl α-sodio-γ-cyanopropylene-α, α, γ-tricarboxylate, is hygroscopic, and absorbs heat when dissolved in water. It gave an oily substance when its aqueous solution was acidified with dilute hydrochloric acid, which was extracted with ether. This ethereal solution was shaken with the aqueous solution of sodium carbonate and the aqueous layer was again acidified and extracted with fresh ether. This second ethereal solution was washed with water, dried with calcium chloride, and evaporated in vacuo. In this way an oily substance was obtained, which gradually crystallised on keeping it in the desiccator. After dried to a constant weight in vacuo in the desiccator it was analysed. 0.2378 Gr. of the substance gave 10.5 c.c. of nitrogen at 24.0° and 758 mm. (Found : N=4.91. $C_{13}H_{17}O_6N$ requires N=4.94%.) According to the mode of formation and the expected result in analysis, this substance is the triethyl γ-cyanopropylene-α, α, γ-tricarboxylate, $C_2H_5OOC(CN)C=CH-CH(COOC_2H_5)_2$.

(1) Cf L. Claisen, *Ann.*, **297** (1897), 1.

This substance has an acid character and dissolves in the aqueous solution of sodium carbonate, evolving carbon dioxide.

It can be induced from the studies on the following cases that the condensation of diethyl ethoxymethylene-malonate with ethyl sodio-cyano-acetate will give the same product as that described above, and there is no difference between triethyl α-cyanopropylene-α, γ, γ-tricarboxylate and triethyl γ-cyanopropylene- α, α, γ-tricarboxylate,

(IV) Diethyl α, α-dicyanopropylene-γ, γ-dicarboxylate. When diethyl ethoxymethylene-malonate was added to the alcoholic solution of sodio-malonitrile a reddish solution was obtained. The solution was filtered from a little amount of solid. The viscous mass which remained after the evaporation of the alcohol was dissolved in water and the solution was shaken with ether to remove substances soluble in ether. On adding dilute hydrochloric acid to the aqueous solution a brown oil separated, which was extracted with ether, but soon from both the aqueous and ethereal solutions colourless crystals separated out. As the colouring impurities were taken into ether, the crystals from aqueous solution were quite colourless, which were collected, washed with cold water and ether, and dried in vacuo over sulphuric acid. 0.1552 Gr. of the substance gave 14.2 c.c. of nitrogen at 23.5° and 760 mm.; 0.2359 gr. of the substance gave 0.4199 gr. of CO_2 and 0.1253 gr. of H_2O. (Found: N=10.23; C=48.56; H=5.94. $C_{11}H_{12}O_4N_2 \cdot 2H_2O$ requires N=10.29: C=48.51; H=5.93%.) This crystalline compound was not the diethyl α, α-dicyanopropylene-γ, γ-dicarboxylate $C_{11}H_{12}O_4N_2$, but the diethyl α, α-dicarbamyl-propylene-γ, γ-dicarboxylate, $(C_2H_5OOC)_2C=CH-CH(CONH_2)_2$. The oily substance which existed for a short time was probably the dinitrile.

When the viscous mass obtained by evaporation of alcohol from the condensation mixture was left in the desiccator for a few days, it took gradually crystalline form. This crystalline substance was twice recrystallised from a small amount of water. 0.3504 Gr. of the substance dried in vacuo over sulphuric acid decreased by 0.0116 gr. on dehydrating at 140−150°. (Found: H_2O=3.31. $C_{11}H_{11}O_4N_2Na \cdot \frac{1}{2}H_2O$ requires H_2O=3.37%.) 0.3388 Gr. of the dehydrated substance gave 34.0 c.c. of nitrogen at 26° and 756 mm. (Fonnd: N=11.02. $C_{11}H_{11}O_4N_2Na$ requires N=10.9%.) According to the mode of formation this is diethyl α-sodio-α, α-dicyanopropylene-γ, γ-dicarboxylate.

(V) Diethyl γ, γ-dicyanopropylene-α, α-dicarboxylate. In the case of the condensation of ethoxymethylene-malonitrile with diethyl sodio-malonate, the resulting solution was not so intensely coloured as in the case of (IV) and the formed sodium compound crystallised easily on evaporating the solvent.

The sodium compound was dissolved in water and dilute hydrochloric acid was added. A brown oily substance deposited at once, but, on stirring, dissolved again in the mother liquor and soon colourless crystalline substance separated out, which was collected, washed with a small amount of water several times and dried in vacuo over sulphuric acid. 0.2596 Gr. of the substance gave 24.5 c.c. of nitrogen at 27.5° and 758.4 mm. (Found: N=10.31, $C_{11}H_{12}O_4N_2 \cdot 2H_2O$ requires N=10.29%.)

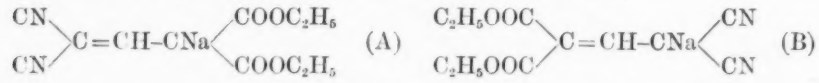
The compound obtained in this case was also a diamide. The constitution should be $(H_2NCO)_2C=CH-CH(COOC_2H_5)_2$, the isomer of $(C_2H_5OOC)_2C=CH-CH(CONH_2)_2$ described in (IV).

Recrystallised from alcohol, the sodium compound became nearly colourless crystals. 0.5245 Gr. of the substance dried at 150° gave 0.1413 gr. of Na_2SO_4. 0.3220 Gr. of the substance dried at 150° gave 32.5 cc. of nitrogen at 27° and 757 mm. (Found: Na=8.72; N=11.03. $C_{11}H_{11}O_4N_2Na$ requires Na=8.92; N=10.9%.) The sodium compound crystallised from water contains half a molecule of water. 0.3440 Gr. of the substance decreased by 0.0113 gr. on dehydrating at 140–150°. (Found: H_2O=3.29. $C_{11}H_{11}O_4N_2Na \cdot \frac{1}{2}H_2O$ requires H_2O=3.37%.) According to the mode of formation this is diethyl *α*-sodio-*γ*, *γ*-dicyanopropylene-*α*, *α*-dicarboxylate.

Considered from the mode of formation the two kinds of diamides described in (IV) and (V) may differ in the position of the double union only. But as it is expectable from the fact that the *α*- and *γ*-positions in glutaconic acid are the same,[1] these two diamides have been found identical. The one, the other, and their mixture melted at the same point 139-140°, solidified then and gradually decomposed when heating was continued.

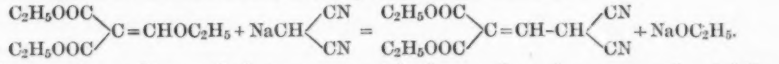
The coincidence in composition (water of crystallisation) of the sodium derivatives of diethyl *α*, *α*-dicyanopropylene-*γ*, *γ*-dicarboxylate and of diethyl *γ*, *γ*-dicyanopropylene-*α*, *α*-dicarboxylate suggested the identity of these two sodium compounds. Really they have been found identical. These two specimens of sodium compounds and their mixture melted at the same point 238–239° (not corr.). It is no wonder that the specimens of the identical sodium compounds gave the identical diamides.

For the identity of the *α*- and *γ*-positions in glutaconic acid $HOOCCH=CH-CH_2COOH$, it is necessary that at least one of the methylene hydrogen atoms remains unsubstituted. There exists, however, no mobile hydrogen atom in the sodium compounds as shown by the formulæ,



(1) J. F. Thorpe, *J. Chem. Soc.* **87** (1905), 1669.

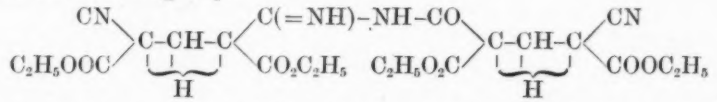
The compound represented by (A) can not be identical with the compound represented by (B). Therefore the constitution of the sodium compounds formed through two ways of condensation must be limited to either of them. Whichever formula it may possess, how two ways of condensation led to the same product can be explained on the assumption that the condensation of an ethoxymethylene compound with a sodium compound proceeds in two stages. In the first stage sodium ethylate is split off from the ethoxymethylene compound and the sodium compound, for instance,



And then the sodium ethylate reacts with the methenyl compound, yielding the sodium derivative of the methenyl compound and alcohol. Now, the methenyl compound formed intermediately has the mobile hydrogen atom, and there is no difference between α- and γ-positions. Thus the condensation of diethyl ethoxymethylene-malonate with sodio-malonitrile and the condensation of ethoxymethylene-malonitrile with diethyl sodio-malonate will give the same intermediate compound, and the second stage of the condensation, where the mobile hydrogen atom is replaced by sodium, will be the same.

The identity of the diamides may not be directly due to their glutaconic structure, but to the identity of the sodium derivatives; and the fundamental cause of the identity of the sodium compounds lies in their glutaconic structure. Although it is not yet decided whether the constitution of the sodium compound is (A) or (B) it can be safely said that the diamide $C_{11}H_{16}O_6N_2$ is the diethyl α, α (= γ, γ)-dicarbamylpropylene-γ, γ (= α, α)-dicarboxylate.

(VI) Diethyl α, γ-dicyanopropylene-α, γ-dicarboxylate. That the condensation of ethyl ethoxymethylene-cyanoacetate with ethyl sodio-cyanoacetate gave the same substance as that synthesized from ethyl cyanoacetate, chloroform, and sodium ethylate, was explained in the previous paper.[1] The constitutional formula previously given to the diethyl dicyanoglutaconate semihydrate can now be written in a more expanded form, for it has become known that the double bond of the propylene nucleus is not fixed. Thus in the following way:



or in any other ways in which the propylene nucleus has a symmetrical structure.[2]

(1) This journal **2** (1927), 240.
(2) Cf. J. F. Thorpe, *J. Chem. Soc.*, **87** (1905) 1669.

(VII) **Ethyl *α*, *α*, *γ*-tricyanopropylene-*γ*-carboxylate.** The sodium derivative of this compound was obtained in coloured crystalline mass by the evaporation of alcohol from the red solution which resulted on adding ethyl ethoxymethylene-cyanoacetate to the alcoholic sodio-malonitrile. As this sodium compound was very easily soluble in water, alcohol, acetone, ethyl acetate, and pyridine, it was not recrystallised in fear of the loss of the substance. The crystalline mass was washed with ether, dried, and dissolved in cold water. On adding hydrochloric acid to the aqueous solution and rubbing the wall of the vessel with a glass rod, a crystalline precipitate in yellowish brown colour separated out, which was collected, washed with water, and dried in the desiccator. 0.1892 Gr. of the substance dried at 100° gave 36.1 c.c. of nitrogen at 22.5° and 751 mm. 0.2953 Gr. of the substance gave 0.5874 gr. of CO_2 and 0.1071 gr. of H_2O. (Found: N=21.20; C=54.27; H=4.06. $C_9H_7O_2N_3 \cdot \frac{1}{2}H_2O$ requires N=21.21; C=54.54; H=4.04%.) The obtained substance corresponded in composition to ethyl *α*, *α*, *γ*-tricyanopropylene-*γ*-carboxylate *semihydrate*. This specimen was yellowish brown and melted at about 190°.

In order to investigate whether this substance is identical with that obtained in the case of (VIII), the sodium compound prepared by another experiment was recrystallised three times from water, when it was obtained as greyish violet crystals. 0.5428 Gr. of the substance decreased by 0.0433 gr. on dehydrating at 130–140°% (Found: H_2O=7.98. $C_9H_6O_2N_3Na \cdot H_2O$ requires H_2O=7.86%.) The aqueous solution of this coloured sodium compound gave light green crystals of the semihydrate of the free nitrile-ester on acidifying.

When the sodium compound was dissolved by heating in a saturated aqueous solution of sodium chloride, the solution separated into two layers. The crystals which separated on cooling the solution in two layers were twice recrystallised from hot water. In this way nearly colourless crystals were obtained, which gave the light yellow semihydrate. This yellow specimen was probably the purest, but the colouring impurities in the brown or green specimen had nearly no perceptible effect on the melting point and the analytical results.

(VIII) **Ethyl *α*, *γ*, *γ*-tricyanopropylene-*α*-carboxylate.** By an analogous procedure the sodium derivative was obtained. This substance was easily soluble in water, acetone, ethyl acetate, and pyridine. On acidifying the aqueous solution of the sodium compound yellow crystalline substance precipitated, which was collected, washed with water, and dried in the desiccator. 0.1490 Gr. of the substance (no decrease in weight when dried at 120–130°) gave 27.7 c.c. of nitrogen at 22.5° and 755 mm. 0.1842 Gr. of the substance gave 34.6 c.c. of nitrogen at 23.5° and 754 mm. 0.2370 Gr. of the

substance gave 0.4710 gr. of CO_2 and 0.0868 gr. of H_2O. 0.3022 Gr. of the substance gave 0.5991 gr. of CO_2 and 0.1100 gr. of H_2O. (Found: N=20.77, 20.83; C=54.22, 54.08; H=4.10, 4.07. $C_9H_7O_2N_3 \cdot \frac{1}{2}H_2O$ requires N=21.21; C=54.54; H=4.04%.) Decided from the analytical results this specimen was not pure and melted gradually by the time when the temperature reached 185°.

To obtain a pure specimen the preparation was repeated, when the sodium compound became quite colourless on recrystallising it twice from hot water. 0.3111 Gr. of the substance decreased by 0.0250 gr. on dehydrating at 130–140°. (Found: H_2O=8.04. $C_9H_6O_2N_3Na \cdot H_2O$ requires H_2O=7.86%.) 0.2861 Gr. of the dehydrated substance gave 52.8 c.c. of nitrogen at 28.5° and 752.3 mm. (Found: N=19.88. $C_9H_6O_2N_3Na$ requires N=19.91%.) This purified sodium compound was transformed into the semihydrate of the free nitrile-ester. 0.1423 Gr. of the substance dried at 120° gave 27.4 c.c. of nitrogen at 27.5° and 759 mm. (Found: N=21.44. $C_9H_7O_2N_3 \cdot \frac{1}{2}H_2O$ requires N=21.21%.)

The semihydrate in (VII) stands in the same relation to the semihydrate in (VIII) as the diamide in (IV) to the diamide in (V). The yellow purest specimen of the semihydrate described in (VII), the yellow semihydrate from the purified sodium compound described in (VIII), and their mixture melted exactly at the same point 190° (corr.). The sodium derivatives obtained through two ways of condensation also coincided in water of crystallisation, and proved to be identical. These two specimens and their mixture melted at the same point 241–242° (not corr.). An analogous discussion may be made on these compounds, and it may be said that the compound obtained from the sodium derivative is the semihydrate of ethyl α, α, γ (= α, γ, γ)-tricyanopropylene-γ (= α)-carboxylate, and its constitution is represented by the formula $(C_8H_7O_2N_2)$–CO–NH–C(=NH)–$(C_8H_7O_2N_2)$.

(IX) $\alpha, \alpha, \gamma, \gamma$-Tetracyanopropylene. Soon after the addition of ethoxymethylene-malonitrile to the alcoholic solution of sodio-malonitrile, fine crystals separated out until the solution was filled with them, which were collected and recrystallised from hot water. In this way colourless fine needles of the sodium derivative of $\alpha, \alpha, \gamma, \gamma$-tetracyanopropylene were obtained, which had one molecule of water of crystallisation. 0.6551 Gr. of the substance decreased by 0.0648 gr. on heating at 135–140°. (Found: H_2O=9.89. $C_7HN_4Na \cdot H_2O$ requires H_2O=9.89%.) 0.1327 Gr. of the dehydrated substance gave 40.5 c.c. of nitrogen at 22.5° and 756 mm. (Found: N=34.14. C_7HN_4Na requires N=34.15%.)

The alcoholic mother liquor of the crystallised condensation product gave a crystalline mass on evaporating it to dryness. The solid which remained undissolved when this crystalline mass was treated with hot water, was recrystallised from alcohol. 0.1581 Gr. of the substance gave 43.2 c.c. of nitrogen at 23.5° and 752 mm. 0.1138 Gr. of the substance gave 30.3 c.c. of nitrogen at 23° and 752.5 mm. (Found : N=30.21, 29.55%.) This substance did not contain sodium, was not changed by treating with dilute hydrochloric acid, and melted at 211–212° without decomposition. 0.1133 Gr. of the substance treated with hydrochloric acid gave 30.5 c.c. of nitrogen at 26° and 757 mm. 0.2292 Gr. of the substance gave 0.4836 gr. of CO_2 and 0.0893 gr. of H_2O. 0.2194 Gr. of the substance gave 0.4617 gr. of CO_2 and 0.0860 gr. of H_2O. (Found : N=29.60 ; C=57.56, 57.41 ; H=4.36, 4.39. $C_7H_2N_4 \cdot C_2H_5OH$ requires N=29.78 ; C=57.43 ; H=4.29%.) No investigation was made on the constitution and the mechanism of formation of this compound.

The sodio-tetracyanopropylene seemed to behave in a different manner towards hydrochloric acid. It deposited neither solid nor liquid, when acidified with the acid. The warm aqueous solution of the sodium compound, acidified with hydrochloric acid, gave the crystals of the original sodium compound on cooling. The acidified solution of this compound, after standing for three weeks, also gave the original substance on evaporating to dryness in the desiccator, the desiccator being filled with the fume of hydrochloric acid. But when the acidified solution of the sodium compound was extracted with ether several times and the aqueous layer was evaporated on the water bath, the residue consisted of sodium chloride alone. The ethereal solution was dehydrated with calcium chloride and evaporated in vacuo over sulphuric acid, when colourless crystals remained, which soon decomposed into a brown amorphous substance. Further the following experiment clearly shows the behaviour of the compound in question.

3.640 Gr. ($\frac{1}{5}\frac{1}{6}$ mol.) of sodio-tetracyanopropylene $C_7HN_4Na \cdot H_2O$ were dissolved in water, acidified with hydrochloric acid, and shaken with ether five times. The aqueous layer was separated quantitatively and evaporated on the water bath, when 1.177 gr. of sodium chloride was obtained. The ethereal extracts were evaporated on the aqueous solution of 1.169 gr. ($\frac{1}{5}\frac{1}{6}$ mol) of sodium chloride, so that the solute in the ethereal solution could enter into the aqueous layer as the ether was evaporated. After the disappearance of the ethereal layer, the aqueous solution was evaporated in vacuo in the desiccator in which concentrated sulphuric acid and soda-lime were placed. This solution, on evaporating to dryness, gave 3.643 gr. of sodio-tetracyanopropylene $C_7HN_4Na \cdot H_2O$. This experiment indicates the perfect reversibility of the reaction $C_7HN_4Na + HCl \rightleftarrows C_7H_2N_4 + NaCl$, and the distinct

existence of the compound $C_7H_2N_4$ which matches hydrochloric acid in strength.

The equilibrium state in the aqueous solution containing C_7HN_4Na, HCl, $C_7H_2N_4$, and NaCl, probably owes its existence to the fact that the compound $C_7H_2N_4$ is soluble in water and has no tendency of combining with water and forming an insoluble substance as in the cases of other nitrile-esters of the dicarboxyglutaconic acid.

Triethyl cyanocarboxyglutaconate is so strong in acidity that it decomposes carbonates, forming its own salt, and tetracyanopropylene matches hydrochloric acid. The continued investigation on the acid character of the latter will bring some interesting results.

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